Experimental report

03/05/2016

Proposal:	**6-03-436**	**Council:**	4/2015
Title:	QENS on the Protic Ionic Liquid Triethylammonium Triflate		
Research area:	Physics		

This proposal is a new proposal

Main proposer:	**Jan P EMBS**
Experimental team:	Juan Francisco MORA CARDOZO Jan P EMBS
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Samples: Triethylammonium triflate

Instrument	Requested days	Allocated days	From	To
D7	12	12	03/11/2015	15/11/2015

Abstract:

Protic Ionic Liquids (PILs) are produced by combining a Brønsted acid and a Brønsted base. The main advantages of PILS for electrochemical applications arise from their anhydrous proton conductivity.The proton transfer from the acid to the base leads to the presence of proton-donor and -acceptor sites and hence of fast fluctuating hydrogen-bond network. However the dynamics of this charge carrier has not been entirely clarified yet. With this proposal we aim to shed light on the proton dynamics in the PIL triethylammonium triflate. The aim of the proposed experiments is to separate coherent and incoherent scattering contributions and thus to allow for a detail analysis of the extra dynamics observed in the partially deuterated PIL sample. We aim to study the T-dependence of both scattering contributions.

In addition to the partially deuterated sample we also will investigate a completely protonated sample.

QENS on the protic ionic liquid Triethylammonium Triflate

Proposal No.: 6–03–436

Experimental team: [1]J.F. Mora Cardozo, [1]Jan P. Embs
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Instrument: D7 **Date:** 02.11.15 – 16.11.15
Instrument Responsible: Andrew Wildes

We present results of the experiments aiming the separation of coherent and incoherent scattering contributions of the (completely protonated) protic ionic liquid Triethylammonium Triflate (p–TEA-TF) $[NH(C_2H_5)_3]^+[SO_3CF_3]^-$ and a partially deuterated version of it (d-TEA-TF) $[NH(C_2D_5)_3]^+[SO_3CF_3]^-$. The chopped neutron beam wavelength was set to 5.7 Å and the beam was polarised in z-direction with a 1:1 non-spin-flip, spin-flip count repeater.

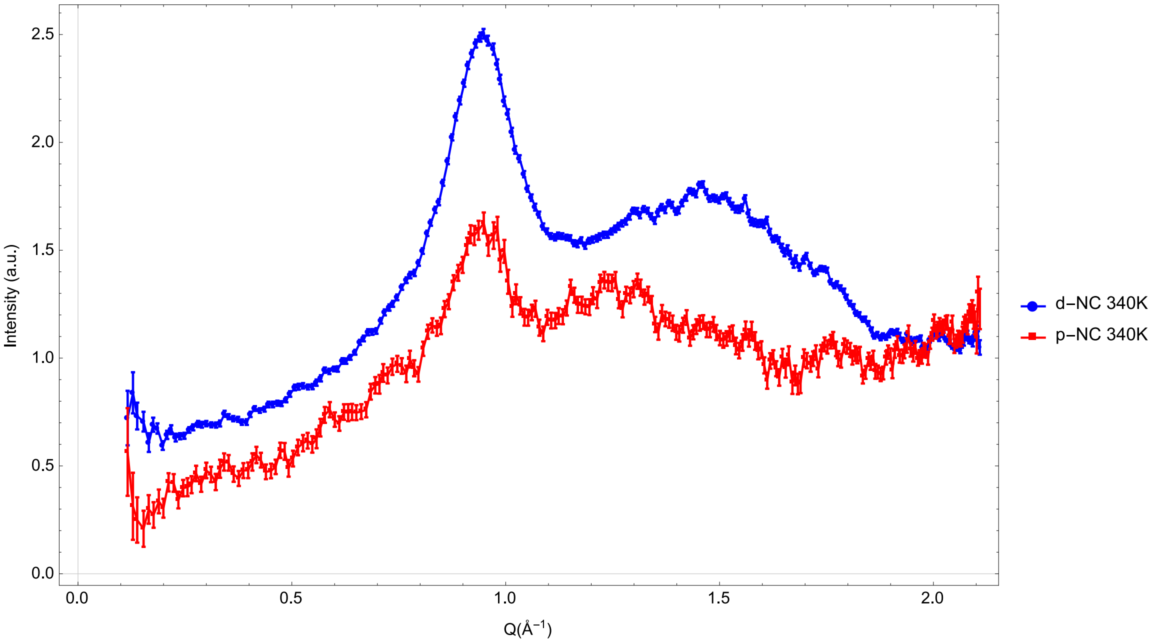

Figure 1: Neither normalised nor Placzek–corrected I(Q)–data (nuclear coherent (NC) contribution) measured at **D7** on **TEA-TF** (red) and **d-TEA-TF** (blue) at 340 K.

The energy resolution at 5.7 Å was 90 µeV(FWHM). The accessible energy transfer range in our experiments was ±1.4 meV, allowing us to access a time-window of the order of some picoseconds; the momentum transfer range was (0.3–2.0) $Å^{-1}$. The measured I(Q) for the two samples is presented in Fig.1.

The fully protonated cation (p-TEA) and the partially deuterated cation (d-TEA) dominate the coherent scattering signal of the complete PILs, however it is worth to highlight that the impact of the anion on the coherent scattering signal isn't the same for each sample. The coherent scattering signal share for the protonated sample is around 70% TEA to 30% TF against the 80% to 20% in the partially deuterated sample. The incoherent scattering from our samples comes almost just from the two different cations; in this fashion we can approximate the incoherent dynamical structure factor measured as the one due to the cation and ignoring the anion contribution. $S_i(Q, \omega)$ is comprised by the system's global diffusion and a contribution from internal molecular motions of the cation. The incoherent structure factor is given as the convolution of the global dynamics and the various localized dynamics:

$$S_i(Q,\omega) = S_{\text{global}}(Q,\omega) \otimes S_{\text{local}}(Q,\omega) \tag{1}$$

The long range dynamic (i.e. the global contribution) is well described by Fick's diffusion and hence by a Lorentzian function with the half-width-half-maximum providing us the effective self-diffusion coefficient. The local contribution is in general given by the following expression:

$$S_{\text{local}}(Q,\omega) = A_0\delta(\omega) + \sum_{n=1}^{N} A_n\mathcal{L}(\Gamma_n) \tag{2}$$

The observed scattering function is the convolution of $S_i(Q,\omega)$ with the instrumental resolution $R(Q,\omega)$ function plus a background (if needed) summarising all motions faster than the observation window fixed by the resolution:

$$S_{\text{observed}}(Q,\omega) = F\left(A_0\ \mathcal{L}(\Gamma_{\text{global}}) + (1-A_0)\,\mathcal{L}(\Gamma_{\text{global}}+\Gamma_n)\right) \otimes R(Q,\omega) + B \tag{3}$$

F is a scaling factor that also contains the Debye-Waller factor. The approach in eqn.3 was employed to separate the various dynamics in the spectra for each sample. To fit the nuclear spin–incoherent (NSI) contribution in d–TEA–TF data, one single Lorentzian reproduced the data, whereas and for p–TEA–TF two Lorentzian functions were used to fit the corresponding scattering contribution; one Lorentzian describes the global dynamics of the system and the second one summarises fast localized processes. The following table shows the values for the corresponding diffusion coefficients:

	NSI		**NC**
T(K)	TEA-TF	d-TEA-TF	d-TEA-TF
320	2.75 ± 0.10	2.21 ± 0.16	2.01 ± 0.07
340	3.66 ± 0.16	2.84 ± 0.18	2.60 ± 0.10
360	4.64 ± 0.16	3.70 ± 0.20	3.31 ± 0.07
380	5.79 ± 0.25	4.63 ± 0.25	4.30 ± 0.15

Table 1: Diffusion coefficients for p–TEA–TF and its partially deuterated version; the diffusion coefficients are given in units of 10^{-10} m^2 s^{-1}.

We present here preliminary results, the data analysis is not yet completed and is still a work in progress!

References

[1] Tatsiana Burankova, Rolf Hempelmann, Verlaine Fossog, Jacques Ollivier, Tilo Seydel, and Jan P. Embs. Proton diffusivity in the protic ionic liquid triethylammonium triflate probed by quasielastic neutron scattering. *The Journal of Physical Chemistry B*, 119(33):10643–10651, 2015. PMID: 26207379.

[2] Tamar L Greaves and Calum J Drummond. Protic ionic liquids: properties and applications. *Chemical reviews*, 108(1):206–237, 2008.